Microstructure and Optical Properties of BaMoO₄ (M = Mo, W) Particles Synthesized by Microwave-Assisted Metathetic Method†

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The BaMoO₄ (M = Mo, W) particles have been synthesized successfully by a cyclic microwave-assisted metathetic method followed by heat-treatment. Well-crystallized BaMoO₄ (M = Mo, W) particles with a fine and octahedron-like morphology and the particle size of 1-2 μm have been formed after annealing at 600 °C for 3 h. The synthesized BaMoO₄ (M = Mo, W) particles have been characterized by X-ray diffraction and scanning electron microscopy. The optical properties have been investigated by photoluminescence emission and Raman spectroscopy.

Keywords: BaMoO₄ (M = Mo, W), Microwave-assisted metathetic method, Luminescence, Raman spectroscopy.

INTRODUCTION

Metal molybdates and metal tungstates have attracted considerable attention for potential applications in photoluminescence, scintillators, photocatalyst hosts for lanthanide-activated lasers and humidity sensors^{1,2}. Several processes have been developed over the past decade to enhance the applications of metal tungstates and metal molybdates prepared by a range of processes, such as co-precipitation³, a solvothermal method⁴, spray pyrolysis⁵, wet chemical method⁶, a mechano-chemical method⁷, a molten salt method⁸, a hydrothermal method⁹, microwave synthesis¹⁰ and a solid-state metathetic reaction¹¹. The microwave heating is delivered to the surface of the material by radiant and/or convection heating, which is transferred to the bulk of the material *via* conduction¹². For practical application of photoluminescence in such products as lasers, three-dimensional displays, light-emitting devices and biological detectors, features such as homogeneous particle size distribution and morphology need to be well defined.

The microwave-assisted metathetic (MAM) technique is one of the most powerful method employed for the crystallization of various unique nanoparticles^{13,14}. Ethylene glycol, as a polar solvent with a relatively high boiling point of 197 °C, is a good candidate for the MAM process. When ethylene

glycol is used as a solvent, the reactions are produced at the temperatures near the boiling point of ethylene glycol. The microwave radiation is supplied to the ethylene glycol so that the components dissolving in the ethylene glycol are capable of coupling with the radiation. When a large amount of microwave radiation is applied into the ethylene glycol, the charged particles are vibrated in the electric field interdependently. Therefore, it is possible to achieve rapid and uniform heating of microwave dielectric materials. An MAM process using ethylene glycol as a solvent is a convenient process that provides a high-qualified yield with a cost-effective balance and for short time periods. In this study, BaMoO₄ (M = Mo, W) particles were synthesized using an MAM reaction in ethylene glycol. The characteristics of the MAM reaction of BaMoO₄ (M = Mo, W) particles are discussed in detail. The final BaMoO₄ (M = Mo, W) products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical properties of the oxide were examined by photoluminescence (PL) emission and Raman spectroscopy.

EXPERIMENTAL

Appropriate stoichiometric amounts of BaCl₂·2H₂O and Na₂MoO₄·2H₂O for BaMoO₄ and BaCl₂·2H₂O and Na₂WO₄·2H₂O for BaWO₄ and ethylene glycol of analytical

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reagent grade were used. To prepare BaMoO_4 1 mol % $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ with 1 mol % $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol. The solutions were mixed and adjusted to pH 9.5 using NaOH. The solutions were stirred at room temperature. Then, the mixtures were transferred into 120 mL Teflon vessels. Each Teflon vessel was placed into a microwave oven operating at the frequency of 2.45 GHz with the maximum output power of 1250 W for 23 min. The working cycle of the MAM reaction was been controlled precisely between 30 s on and 30 s off for 8 min, followed by further treatment of 30 s on and 60 s off for 15 min. The resulted powder samples were treated with ultrasonic radiation and washed many times with hot distilled water. The white precipitates were collected and dried at 100 °C in a drying oven. After this, the final products were heat-treated at 600 °C for 3 h.

The phase composition of final powder products formed after the cyclic MAM reaction and following heat-treatment was identified using XRD (D/MAX 2200, Rigaku, Japan). The microstructures and surface morphologies of the BaMoO_4 (M = Mo, W) particles were observed using SEM/EDS (JSM-5600, JEOL, Japan). Their photoluminescence spectra were recorded at room temperature using a spectrophotometer (Perkin Elmer LS55, UK). Raman spectroscopy measurements were performed using a LabRam HR (Jobin-Yvon, France) device. The 514.5-nm line of an Ar-ion laser was used as an excitation source and the power on the samples was kept at 0.5 mW.

RESULTS AND DISCUSSION

The XRD patterns recorded from the synthesized BaMoO_4 and BaWO_4 particles are shown in Figs. 1 and 2. All the diffraction peaks were assigned to the tetragonal-phase BaMoO_4 and BaWO_4 , which were in good agreement with the crystallographic data of BaMoO_4 (JCPDS: 29-01930) and BaWO_4 (JCPDS: 43-0646). The BaMoO_4 formed had a Scheelite-type crystal structure with lattice parameters of $a = b = 5.573 \text{ \AA}$ and $c = 12.786 \text{ \AA}$ ¹³ and the BaWO_4 formed had the same crystal structure with lattice parameters $a = b = 5.613 \text{ \AA}$ and $c = 12.720 \text{ \AA}$ ¹. The result confirms that the BaMoO_4 and BaWO_4 particles can be prepared using the cyclic MAM route. The post-synthesis heat-treatment plays an important role in forming well-defined crystallized micromorphology. To achieve such morphology, the BaMoO_4 and BaWO_4 particles need to be heated at 600 °C for 3 h. This suggests that the cyclic MAM route, in combination with subsequent heat-treatment, is a suitable way for the formation of BaMoO_4 and BaWO_4 particles with well developed high-intensity peaks from the (112), (200) and (312) planes, which are the major peaks of BaMoO_4 and BaWO_4 .

The SEM images of the synthesized BaMoO_4 and BaWO_4 particles are shown in Fig. 3(a-b). The as-synthesized samples have a well-defined and octahedron-like morphology with the particle size of 1-2 μm . The MAM reactions, such as $\text{BaCl}_2 + \text{Na}_2\text{MoO}_4 \rightarrow \text{BaMoO}_4 + 2\text{NaCl}$ and $\text{BaCl}_2 + \text{Na}_2\text{WO}_4 \rightarrow \text{BaWO}_4 + 2\text{NaCl}$, involve the exchange of atomic/ionic species, in which the driving force is the exothermic reaction accompanying the formation of NaCl ^{13,14}. BaMoO_4 (M = Mo, W) particles were heated rapidly and uniformly by the cyclic MAM route. This classifies the method among simple and cost-effective ones and, evidently, the MAM technology

Fig. 1. XRD patterns of the synthesized BaMoO_4 particles

Fig. 2. XRD patterns of the synthesized BaWO_4 particles

Fig. 3. SEM images of the synthesized (a) BaMoO_4 and (b) BaWO_4 particles

is able to provide high yields with an easy scale-up as a viable alternative for the rapid synthesis of complex oxide compounds¹⁵.

Fig. 4(A-B) show the photoluminescence emission spectra of the BaMoO_4 and BaWO_4 particles after heat-treatment at (a) 400 °C, (b) 500 °C and (c) 600 °C for 3 h excited at 250 nm at room temperature. The emission spectra of metal molybdates and tungstates are due mainly to charge-transfer transitions within the $[\text{MoO}_4]^{2-}$ and $[\text{WO}_4]^{2-}$ complex^{16,17}. With the excitation at 250 nm, BaMoO_4 particles in Fig. 4(A) exhibit photoluminescence emission over the blue wavelength range of 390-420 nm. The four narrow shoulders in the emission spectra at approximately 490, 510, 520 and 610 nm are believed to be due to a defect structure¹⁸. All the spectra show broad peaks with several considerable superimposed fine structures. With excitation at 250 nm, BaWO_4 particles in Fig. 4(B) exhibit major photoluminescence emissions in the blue wavelength range of 390-420 nm. The emission spectra of

Fig. 4. Photoluminescence emission spectra of the synthesized (A) BaMoO₄ and (B) BaWO₄ particles after heat-treatment at (a) 400 °C, (b) 500 °C and (c) 600 °C for 3 h excited at 250 nm at room temperature

four narrow shoulders at approximately 490, 510, 520 and 600 nm are considered to be generated by defect structures. The explanation of the narrow shoulders in Fig. 4(A-B) is proposed considering the Jahn-Teller splitting effect^{19,20} on excited states of [MoO₄]²⁻ and [WO₄]²⁻ anions in BaMoO₄ and BaWO₄. This is similar to that reported by Zhang *et al.*²¹. The Jahn-Teller splitting effect essentially determines the shape of emission of the MMoO₄ (M = Ba, Ca) particles¹³. The additional emission bands can be interpreted by the existence of Frenkel defect structures (oxygen ion shifted to the interposition with the simultaneous creation of vacancy) in the surface layers of the BaMoO₄ and BaWO₄ particles^{22,23}. The photoluminescence spectra of the BaMoO₄ and BaWO₄ prepared from 400–600 °C had same peak positions. The photoluminescence intensities of the samples prepared at 600 °C for the BaMoO₄ and BaWO₄ particles are much stronger than those of the samples prepared at 400 and 500 °C. It is noted that the high crystallinity plays an important role in the improvement of luminescent efficiency. Therefore, it can be considered that the enhancement of photoluminescence intensity with the heat-treatment temperature up to 600 °C is due to the increment of crystallinity.

Raman spectra of the BaMoO₄ and BaWO₄ particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW are shown in Fig. 5(a-b). The vibration modes in the Raman spectra of molybdates and tungstates are classified into two groups, internal and external. The internal vibrations are related to the [MoO₄]²⁻ and [WO₄]²⁻ molecular group with a stationary mass center. The external vibrations or lattice phonons are associated to the motion of the Ba²⁺ cation and rigid molecular units. In free space, [MoO₄]²⁻ and [WO₄]²⁻ tetrahedra show T_d-symmetry. Raman modes for the BaMoO₄ particles in Fig. 5(a) were detected as ν₁(A_g), ν₃(B_g), ν₃(E_g), ν₄(E_g), ν₄(B_g) and ν₂(B_g) vibrations at 893, 840, 793, 361, 346 and 327 cm⁻¹, respectively, which provide evidence of a Scheelite structure. The free rotation mode was detected at 191 cm⁻¹ and the external modes were localized at 140–107 cm⁻¹. Raman modes for the BaWO₄ particles in Fig. 5(b) were detected as ν₁(A_g), ν₃(B_g), ν₃(E_g), ν₄(E_g), ν₄(B_g) and ν₂(B_g) vibrations at 925, 831, 795, 352, 344 and 332 cm⁻¹, respectively, which provide evidence of a Scheelite structure. The free rotation mode was detected at 189 cm⁻¹ and the external modes were localized at 148 cm⁻¹. The well-resolved sharp peaks for the BaMoO₄ and BaWO₄ particles indicate that the synthesized particles are highly crystallized. The type of cations (Ca²⁺, Sr²⁺, Ba²⁺) can influence on the Raman modes by changing the size of the crystal unit cell and by a covalent cation effect²⁴.

Fig. 5. Raman spectra of the synthesized (a) BaMoO₄ and (b) BaWO₄ particles excited by the 514.5 nm line of an Ar-ion laser at 0.5 mW on the sample

Conclusion

The BaMoO₄ (M = Mo, W) particles showed a fine and octahedron-like morphology, and the particles with size of 1–2 μm have been formed by the MAM method. With excitation at 250 nm, the BaMoO₄ and BaWO₄ particles exhibit major photoluminescence emissions over the blue wavelength range of 390–420 nm. The photoluminescence intensities of the BaMoO₄ and BaWO₄ particles prepared at 600 °C were much stronger than those of the samples prepared at 400 and 500 °C. Raman modes of the BaMoO₄ particles were detected at 893, 840, 793, 361, 346 and 327 cm⁻¹ and the Raman modes of the BaWO₄ particles were detected at 925, 831, 795, 352, 344 and 332 cm⁻¹.

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